Non-perturbative J_{pd} model and ferromagnetism in dilute magnets

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We calculate magnetic couplings in the J_{pd} model for dilute magnets, in order both to identify the relevant parameters which control ferromagnetism and also to bridge the gap between first principle calculations and model approaches. The magnetic exchange interactions are calculated non-perturbatively and disorder in the configuration of impurities is treated exacly, allowing us to test the validity of effective medium theories. Results differ qualitatively from those of weak coupling. In contrast to mean field theory, increasing J_{pd} may not favor high Curie temperatures: T_C scales primarily with the bandwidth. High temperature ferromagnetism at small dilutions is associated with resonant structure in the p-band. Comparison to diluted magnetic semiconductors indicate that Ga(Mn)As has such a resonant structure and thus this material is already close to optimality.

The basis of our understanding of magnetism in metals is the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction[1]. The magnetic exchange results from interaction of inner d- or f- localized orbitals and the outer s- or p- that form the conduction bands. In the standard form it is calculated with perturbative treatment of the coupling between the moments and the carriers on a definite Fermi surface, which is itself weakly affected by the presence of the magnetic moments. This leads to successful interpretation of oscillating exchanges in, for example, transition or rare earth metals. However the same concepts are often applied in situations where this perturbative approach is not really applicable. There are many situations where the coupling between moments and itinerant carriers is not weak and it is important to determine changes in magnetic exchange in this regime, for example in the field of manganites[2], double perovskites[3] or in materials modelled by Kondo lattices[4]. In another field of great current interest, diluted magnetic semiconductors (DMS), a belief, incorrect in our view[5], in the applicability of weak coupling has resulted from an unhappy juxtaposition of two approximations: a simplified RKKY view of magnetic interactions and over-simplified molecular field theory for the thermodynamics. This leads to the estimate for the Curie temperature $T_C^{MF} = J_{pd}^2 x n^{1/3}/t$, where $t = 1/m^*$ is the inverse of the effective mass. J_{pd} is the coupling between d-orbital moments and the primarily p-orbital conduction carriers, x the concentration of d-orbitals and n the density of carriers. This estimate has even been influential in the search for new materials: attempts to increase T_c at low doping have focussed on seeking large J_{pd} and small bandwidth (large effective mass). We shall show that the widely used T_C^{MF} is in fact very misleading in the non-perturbative limit. Apart from potential applications [6], these materials are of fundamental interest for exploring ferromagnetism in a regime where geometric disorder is strong (because of the low concentrations of dopants) and the values of J_{pd} are strong. Unfortunately these issues of principle have been obscured by insistence [7] on the weak-coupling picture, and has hidden richer underlying aspects. We argue that these systems are particularly interesting because the ferromagnetism, can *only* be understood if the crucial coupling J_{pd} is treated non-perturbatively. An approach taking *ab initio* estimates of couplings and reliable treatment of the thermodynamics [5] can be successful, but the effective magnetic interactions found, which include a multitude of effects, have not been understood in simple terms. Calculations must be taken for each individual composition. A more systematic approach for finding promising new materials is possible if we have simple but accurate model systems. We can then identify which parameters are important: J_{pd}, the carrier density or the bandwidth of the conducting band? We can also examine assumptions of the *ab initio* approach: e.g. the Coherent Potential Approximation (CPA) for carrier disorder. The method we shall employ makes effective medium approximations *neither* in the deriving of the magnetic couplings *nor* in calculating magnetic properties. Thus an aim is to make a bridge between *ab initio* and conceptually sim-

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pler model approach. A practical question is whether T_C can be increased by choice of other chemical dopants. In lightly doped III-V semiconductors, it will appear that Ga(Mn)As is in fact close to optimal. Here we discuss the theory appropriate to dilute magnets where the dopants provide well defined moments, but the concepts are relevant to a wider class of novel magnets ("d^0" magnets) in which there is no clear distinction between localized magnetic moments and the itinerant carriers of the (doped) host[8, 9].

The J_{pd} model (or dilute Kondo lattice) is of a band of atomic d- orbitals coupled to an itinerant "p-band" of carriers via a Hund's rule coupling. In the manganites, for example, the "p" band is in fact be constructed from e_g orbitals.

$$H = -\sum_{ij,\sigma} t_{ij} c^\dagger_{i\sigma} c_{j\sigma} + \sum_i J_i \mathbf{S}_i \cdot \mathbf{s}_i + \sum_{i\sigma} V_i c^\dagger_{i\sigma} c_{i\sigma} \quad (1)$$

$t_{ij} = t$ for i and j nearest neighbors and zero otherwise. In the exchange between localized impurities spin and itinerant electron gas J_i is a random variable: $J_i = J_{pd}$ and $V_i = V$ if the site i is occupied by a magnetic impurity, and zero otherwise. V_i is here to mimic the effect of chemical substitution that accompanies the presence of the magnetic moment. $\mathbf{S}_i$ is the magnetic impurity spin operator at site i and $\mathbf{s}_i = c^\dagger_{i\alpha}(1/2\boldsymbol{\sigma}_{\alpha\beta})c_{i\beta}$ the spin operator, at the same site, of the itinerant electron gas. The d spins are distributed randomly at low concentration x on a regular lattice, for simplicity taken to be simple cubic. We remark that this model can be extended trivially to include several bands, as would be appropriate for models of double perovskites or manganites, where both the hopping t_{ij} and on-site potentials V_i may be random[10, 11]. The results that will follow are non-perturbative in the J_{pd} coupling and exact in the disorder. A crucial effect that will be seen, and is neglected to low order in perturbation theory, is that as J_{pd} increases, the conduction band is increasingly affected by the presence of the magnetic ions. The calculations are made in the ferromagnetic phase, whose stability is tested *a posteriori*, and therefore start from the configuration of spins S that are fully aligned in some direction $S^z_i = S$ for all occupied i. We can diagonalize in the Hilbert space (spins plus electrons) defined by the fully polarized d-spins provided that we ignore the transverse fluctuations of those spins, of order $\frac{1}{S}$[12]. Thus our theory is exact in the limit of large $S \to \infty$ For the electronic degrees of freedom this leaves a Hamiltonian quadratic in fermion operators. The effect of the d-orbitals is to produce an effective spin-dependent term of $V^{\pm}_i = V \pm \frac{J_{pd}S}{2}$ on each occupied state, i.e. a random site potential for up (+)and down (-) carriers. For each configuration of disorder this Hamiltonian will be diagonalized exactly.

In Fig.1 we show the single particle density of states for fixed $J_{pd}S = 5t$ and concentration $x = 5\%$ of magnetic impurities and different values of the d-orbital potential

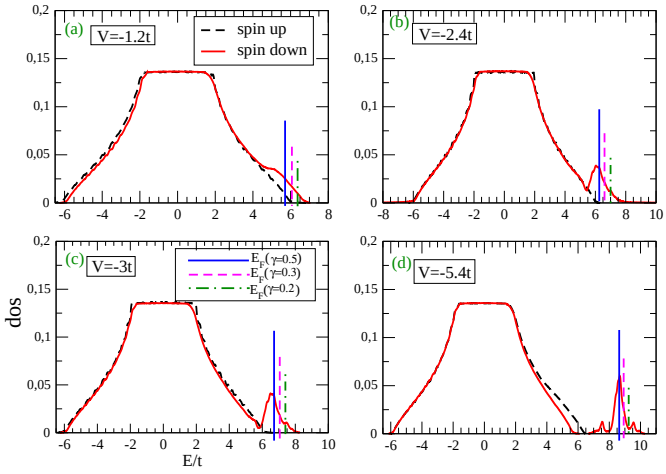

FIG. 1: (Color online) Density of states. The bands of spin down and up are continuous and dashed respectively. Energies are in units of t, $J_{pd}S = 5t$ and the concentration is 5%. The Fermi energy is indicated for three band fillings γ

$V/t = -1.2, -2.4, -3$ and -5.4. The parameters were chosen to reproduce the general form seen in doped III-V semiconductors, as will be discussed in more detail below. For all calculations presented, the systems were sufficiently large (typically $\sim 16^3$ sites) that finite size effects are negligible. As V increases from the smallest value, a well defined impurity band for the minority band splits from the valence band. The Fermi energy is shown for different values of $\gamma = n_h/x$, where n_h denotes the density of holes in a filled band. We will see below how the magnetic couplings are correlated with the form of the density of states and the position of the Fermi energy.

The magnetic exchange interactions are derived at all distances between the different moments from the carrier Green functions $G^{\sigma}_{ii'}$[13]. This defines an effective (dilute) Heisenberg model for the magnetic moments, again valid for spins in the classical limit, $\mathcal{H}_{Heis} = -\sum_{i,j} \mathcal{J}_{i,j} S_i \cdot S_j$. Exchanges are calculated by applying infinitesimal fields to the aligned ferromagnetic state[13].

$$\mathcal{J}_{i,j} = -\frac{1}{\pi} \Im \int_{-\infty}^{E_F} \Sigma_i G^{\uparrow}_{i,j}(\omega) \Sigma_j G^{\downarrow}_{j,i}(\omega) d\omega$$

In this case $\Sigma_i = V^+_i - V^-_i$. We note that the calculations use no effective medium approximation. In Fig. 2(a) we show the couplings averaged over different impurity configurations. We vary the hole doping per d-orbital γ for fixed $x = 5\%$ and $V = -2.4t, J_{pd}S = 5t$ (corresponding to Fig.1(b)). These clearly differ from RKKY for all fillings in that they do not oscillate around a mean value of

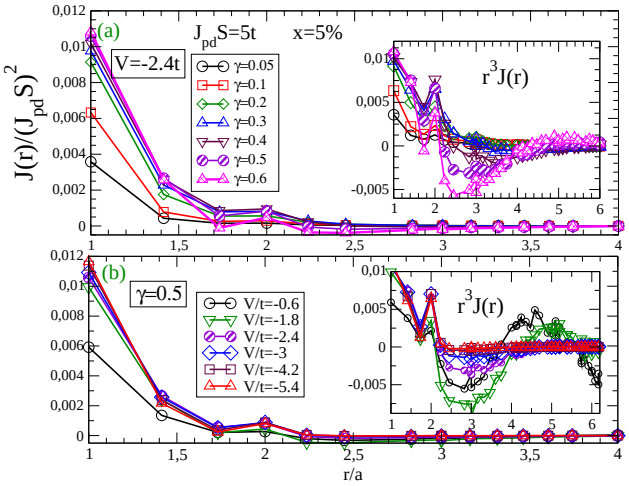

FIG. 2: (Color online) (a)Magnetic exchange as a function of distance, in units of lattice spacing, for different values of γ. Other parameters correspond to case (b) of Fig. 1. (b) Exchanges for different values of the potential V at half filling. In inset, the exchanges rescaled: $J(r)r^3$

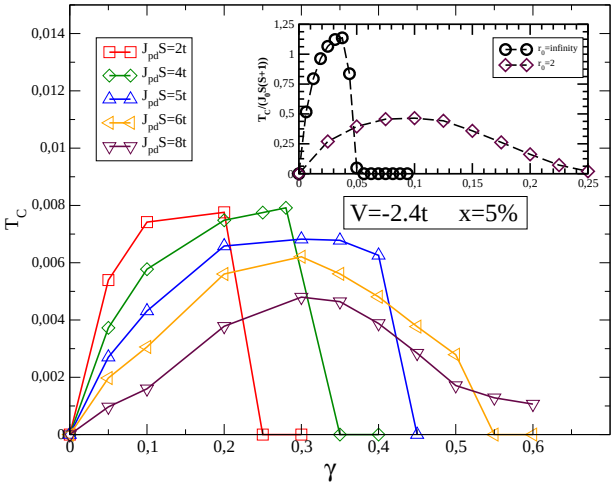

FIG. 3: (Color online) Curie temperature in units of t as a function of carrier density. In insert the same calculation for the RKKY couplings see ref [14] Fig.4

zero and beyond 3 lattice spacings they essentially vanish. While varying sharply with distance they do not change in sign, at least for small γ. The couplings at short distances increase monotonically with γ but for sufficiently large γ antiferromagnetic values appear at larger distances (see inset). In Fig. 2(b) the $J(r)$ with different potentials V are shown for fixed γ. As $|V|$ increases the interactions increase at short distances but become of very short range. For $|V|$ small the longer range oscillations appear clearly, as seen in the inset. Thus from Fig.2 there is a range of V and γ where the couplings are all ferromagnetic ($J(r) \geq 0$). This is associated (see Fig. 1 (b)) with incipient development of a visible impurity band just at the band edge. This ferromagnetic "bias" results from the resonant form of the p-band as advanced in Ref.[14]. In that paper we compared to exchange calculated in a toy model between two resonant states[15], arguing that particle-particle channels responsible for super-exchange should be suppressed. In contrast, in the present calculation there is no artificial separation between the resonant states and the rest of the conduction band nor between different contributions (particle-hole and particle-particle channels). The ideas are coherent in that the J_{pd} acting between the d- spin and the resonant p-state suppress particle-particle virtual states. For the largest values of $|V|$ the clear suppression of exchange for large distances (see inset to Fig. 2(b)) is a precursor to pure magnetic double exchange type[16]. For J_{pd} and V strictly infinite we expect the coupling to reduce to nearest neighbours: $\mathcal{J}_{ij} = t_{ij}\langle c_i^\dagger c_j\rangle$[10] For $J_{pd}S$ finite, however, the exchange interactions extend further than nearest-neighbours[17].

We now calculate the Curie temperatures T_C by the self-consistent local random phase approximation (SC-LRPA)[5] which treats geometric disorder exactly, as is particularly important in the dilute limit. SC-LRPA has been successful in reproducing experimental T_C of DMS and agrees with Monte Carlo simulations[18, 19]. Figs. 3 and 4 shows the Curie temperatures (T_C) as functions of γ and V at half-filling respectively, and various values of J_{pd}. Unlike the predictions of T_c^{MF}, T_C increases monotonically *neither* with J_{pd} *nor* with γ. For $\gamma = 0.1$, for instance, T_C *decreases* with J_{pd}! Large values of J_{pd} are primarily useful in broadening the range of stability of ferromagnetism with γ. For comparison we show in inset previous results in the RKKY regime[14]. At the smallest values of J_{pd} the region of stability (note the difference in scale γ) approaches the RKKY results, as expected. In Fig. 4 we see that T_C is less sensitive to J_{pd} in the large V limit. This is essentially the limit of double exchange. The ferromagnetic bias is essentially the physics of double exchange[20], and the scale of T_C is t. Note we make the assumption that the ferromagnetic T_C calculated with couplings *averaged over configurations* is equal to that obtained, in the thermodynamic limit, with *unaveraged* couplings. We have checked this assumption and it is accurate.

We can use our results as a simple model for doped Ga(Mn)As. We take parameters from photoemission[21] $J_{pd} \approx 1.2eV, S = 5/2, J_{pd}S \approx 3eV$. From the band-structure of GaAs: $m^\star \approx 0.5m_e$, lattice spacing $a_0 = 5.65\mathring{A}$, this gives $t \approx 0.7eV$ and thus $J_{pd} = 4t$. The value of $V/t = -2.4eV$ was chosen to mimic the calculated density of states of Ga(Mn)As. For these parameters and $x = 5\%$, from Figure. 3, we obtain a maximum $T_C^{1band} \approx 65K$ at $\gamma = 0.3$. Because there are two degenerate hole bands and we have neglected all correlations

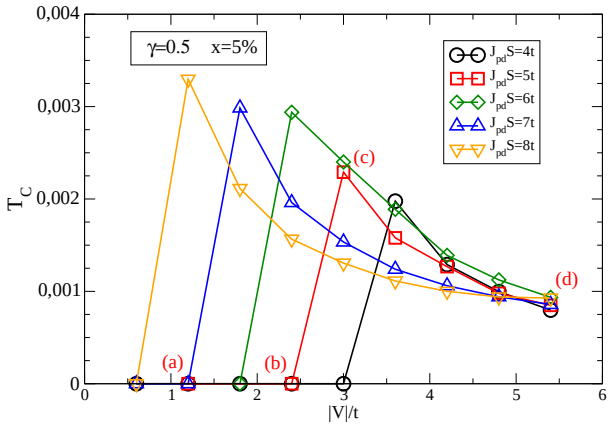

FIG. 4: (Color online) Curie temperature in units of t at half-filling as a function of potential V and varying coupling J_{pd}. Points (a)-(d) correspond to the density of states of Figures 1(a)-(d) respectively

in the p-bands, we can simply extend to 2 independent bands: $T_C^{2band} = 2T_C^{1band} \approx 130K$, close to the measured value in annealed samples of $Ga_{.95}(Mn)_{0.05}As$. This is a crude comparison as the lattice is face-centred cubic and not cubic and, at first sight, the natural concentration to chose for uncompensated samples might be two half-filled bands $\gamma = 0.5$ to give one carrier per dopant. We argue, however that $\gamma = 0.3$ *is* comparable to uncompensated Ga(Mn)As since it is at this doping that the density of states (calculated from band structure[22]) most resembles that of Figure1b, with E_F slightly *above* the maximum in the impurity peak. The apparently remarkable agreement for such a simple model is found for the range of concentrations relevant to experiments. We conclude *if* J_{pd} is treated non-perturbatively we do not need extensions such as the 6-band Luttinger model[7] to give accurate quantitative comparison. We can also understood from the position of the impurity band why Ga(Mn)As has a larger T_C than Ga(Mn)N and In(Mn)As which resemble more cases (d) and (a) of Fig. 1 respectively[5]. Since the estimated J_{pd} and bandwidths for these materials are all very similar, the important difference is the potential V. From the calculated T_Cs shown in the Figures and comparison with the density of states in Fig 1 (b),we see that Ga(Mn)As has close to optimal parameters. This may explain failure to find higher values of T_C in III-V semiconductors without invoking other effects: local clustering or increasing bandwidth.

To conclude, we have shown that in the non-perturbative regime the J_{pd} model has effective magnetic couplings very different from those of RKKY and resemble those of *ab initio* calculations for the DMS. This similarity supports the accuracy of CPA as used in the first principle calculations for calculating magnetic exchanges, an approximation that has often been questioned. While we have presented results in the dilute regime, we note that our approach, which gives the exchange interactions in real space, can be used in more general situations at higher concentrations or with inhomogeneities, as may be applicable in other materials described by the J_{pd} model and its extensions. For dilute magnets a region of parameter space gives couplings that are all ferromagnetic. The reason[14] is made explicit: optimality is associated with a resonant structure seen in the p-band. The potential V must be sufficiently strong that this occurs, but if it is too strong, couplings are too short-range to maintain long range order. Unlike previous mean field theories (T_C^{MF}), the temperature *scale* for ferromagnetism is controlled *not by* J_{pd} but by the bandwidth t. The physics is essentially that of double exchange in this regime. The values of Fermi energy, J_{pd} and the potential shift V are important in obtaining optimal couplings.

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